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(54) **Heat-resistant zinc alloy and molded article thereof**

(57) A heat-resistant zinc alloy exhibiting good creep resistance even at a temperature of not less than 100°C comprises at least one of nickel and manganese in a total amount of not more than 3.5% by weight based on the total weight of the alloy, titanium and/or zirconium by not more than 2%wt, optionally aluminium by not more than 0.5%wt, copper by not more than 2%wt as well as one or more of Cr, Sc, Be, Li, Y and lanthanoids by not more than 0.5%wt in total and the balance of zinc and inevitable impurities. A molded article comprises the heat-resistant zinc alloy defined above. The heat-resistant zinc alloy is excellent in the creep resistance even at a high temperature and thus the heat-resistant zinc alloy can considerably expand the fields of application of the molded articles produced from the alloy.

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Description

[0001] The present invention relates to a creep-resistant zinc alloy and a molded article thereof and more specifically to a heat-resistant zinc alloy exhibiting good creep resistance even at a temperature of not less than 100 °C and a molded article consisting of the heat-resistant zinc alloy.

[0002] Up to this time, the zinc alloy has widely been used for producing parts of motorcars, parts of electrical apparatuses and metallic materials for construction according to the die-casting technique and the zinc alloys used in these applications are mainly composed of zinc-aluminum alloys. These zinc alloys can ensure excellent mechanical strength in the vicinity of room temperature, but they suffer from such a problem that they undergo severe creep at a temperature of not less than 100 °C and therefore, they cannot be used under such severe conditions. Accordingly, this greatly limits the use of die-casting molded article consisting of zinc alloys.

[0003] As zinc alloys developed for solving the foregoing problem, there have been proposed, for instance, heat-resistant zinc alloy substantially free of any aluminum component such as ILZRO 14 (Zn-1.2Cu-0.3Ti-0.02Al) and ILZRO 16 (Zn-1.2Cu-0.3(Ti+Cr)-0.02Al), but there has been desired for the development of a zinc alloy having further improved creep resistance even at a high temperature.

[0004] In general, it is an object of the present invention to develop a heat-resistant zinc alloy which can satisfy the foregoing conventional requirements and which permits the solution of the foregoing problem and more specifically, it is an object of the present invention to provide a zinc alloy which exhibits high strength, good heat-resistant and good creep resistance even at a temperature of not less than 100°C and which can accordingly substantially expand the fields of application of molded articles thereof.

[0005] It is another object of the present invention to provide a molded article consisting of the heat-resistant zinc alloy.

[0006] The inventors of this invention have conducted various investigations to accomplish the foregoing objects, have found that the creep resistance of ILZRO 14 and ILZRO 16 at a temperature of not less than 100°C can significantly be improved by substituting at least one of nickel and manganese for the copper component thereof and have thus completed the present invention.

[0007] According to an aspect of the present invention, there is provided a heat-resistant zinc alloy exhibiting good creep resistance at a temperature of not less than 100 °C , which comprises at least one of nickel and manganese in a total amount of not more than 3.5% by weight on the basis of the total weight of the alloy and the balance of zinc and inevitable impurities.

[0008] Furthermore, the heat-resistant zinc alloy of the present invention may optionally comprise at least one of the following component (a) to (d):

(a) not more than 2% by weight, based on the total weight of the alloy, of copper;

(b) at least one of titanium and zirconium in a total amount of not more than 2% by weight based on the total weight of the alloy;

(c) not more than 0.5% by weight, based on the total weight of the alloy, of aluminum; and

(d) at least one member selected from the group consisting of chromium, scandium, beryllium, lithium, yttrium, lanthanoid and magnesium in a total amount of not more than 0.5% by weight based on the total weight of the alloy.

[0009] According to another aspect of the present invention, there is also provided a molded article which comprises the foregoing heat-resistant zinc alloy.

[0010] Fig. 1 is a graph showing the results of the creep tests (changes in creep strain with time) observed for the zinc alloys produced in Example 1 and Comparative Example 1.

[0011] In the heat-resistant zinc alloy of the present invention, the nickel and/or manganese components improve the creep resistance of the zinc alloy at a temperature of not less than 100 °C . In this respect, it is preferred to use a combination of nickel and manganese since the effect of the addition thereof is higher than that expected when they are used separately. If the total amount of nickel and/or manganese is not more than about 3.5% by weight, they are occluded in the zinc phase to thus reinforce the resulting zinc alloy, but if it exceeds 3.5% by weight, the resulting zinc alloy causes separation of an ϵ -phase and this is liable to make the zinc alloy brittle. Moreover, if the total amount of nickel and/or manganese exceeds 3.5% by weight, the flowability of the molten metal of such an alloy is liable to be considerably impaired and this makes the die casting thereof very difficult. For this reason, at least one of nickel and manganese is added to the heat-resistant zinc alloy of the present invention in a total amount of not more than 3.5% by weight and preferably from 0.7 to 3% by weight.

[0012] The heat-resistant zinc alloy of the invention may optionally comprise copper. The copper component can improve the creep resistance of the resulting alloy at a temperature of not less than 100°C in combination with at least one of nickel and manganese. If the amount of copper incorporated into the alloy is not more than about 2% by weight, it is occluded in the zinc phase to thus reinforce the resulting zinc alloy, but if it exceeds 2% by weight, any further

improvement in the effect of the addition thereof cannot be expected at all and if it exceeds 3% by weight, the resulting zinc alloy causes separation of an ϵ -phase and this is liable to make the zinc alloy brittle. Accordingly, the amount of copper to be incorporated into the heat-resistant zinc alloy of the invention is not more than 2% by weight.

[0013] The heat-resistant zinc alloy according to the present invention may optionally comprise at least one of titanium and zirconium. The titanium and/or zirconium components can significantly improve the creep strength of the resulting zinc alloy, but this effect of these metals reaches its maximum at an added amount of 2% by weight and any further improvement of the effect is not expected. Therefore, the heat-resistant zinc alloy of the present invention may comprise titanium and/or zirconium in a total amount of not more than 2% by weight.

[0014] The heat-resistant zinc alloy of the invention may further comprise, if necessary, aluminum. The addition of aluminum in a small amount on the order of not more than 0.5% by weight is effective for inhibiting any oxidation of the zinc alloy molten metal. For this reason, the zinc alloy of the present invention may comprise aluminum in an amount of not more than 0.5% by weight.

[0015] The heat-resistant zinc alloy of the present invention may optionally comprise at least one member selected from the group consisting of chromium, scandium, beryllium, lithium, yttrium, lanthanoid and magnesium. These alloy components permit the improvement of the mechanical strength of the resulting zinc alloy. However, the addition of these metal components to the zinc alloy in a total amount of more than 0.5% by weight is liable to reduce the impact strength of the resulting zinc alloy. Accordingly, the zinc alloy of the present invention may comprise at least one of these metals in a total amount of not more than 0.5% by weight.

[0016] The heat-resistant zinc alloy of the present invention is favorable for the cold chamber die casting, thixotropic casting and injection molding. Moreover, the zinc alloy of the present invention may likewise be applied to the usual sand molding, die casting, low pressure casting and various kinds of precision investment casting. The molded article of the present invention can be produced according to these casting techniques. The term "thixotropic casting (thixocasting)" herein used means a method which comprises the steps of precast-forming a raw zinc alloy in a cylinder of an injection molding machine such as that disclosed in Japanese Examined Patent Publication No. Hei 2-15620; realizing a thixotropy condition thereof under the influence of the shearing action by the screw of the machine to thus form an article. In addition, the term "injection molding technique" used herein is similar to the thixocasting method and means a method comprising the steps of heating a raw zinc alloy at a temperature of immediately above the melting point of the alloy and casting the alloy in its molten condition.

[0017] The heat-resistant zinc alloy of the invention can be molded, for instance, by hot chamber die casting, cold chamber die casting, injection molding, thixocasting.

[0018] The present invention will hereinafter be described in more detail with reference to the following working Examples, but the present invention is not restricted to these specific Examples at all.

Examples 1 to 16 and Comparative Examples 1 to 3

[0019] Electrolytic zinc as a base metal, and desired amounts of Ni, Mn, Cu, Al, Ti, Zr, Cr, Sc, Be, Li, Y, lanthanoid (Mishmetals, Mm) and/or Mg were introduced into a graphite crucible. The metals, i. e., Ni, Mn, Cu, Al, Ti, Zr, Cr, Sc, Y, Mm and/or Mg were added to the crucible in the form of a master alloy, while Li and Be were directly added to the crucible and these metals were molten to thus prepare zinc alloys each containing the alloy components listed in the following Table 1 in amounts (% by weight) given in Table 1 and the balance of zinc and inevitable impurities. In this regard, the zinc alloy of Comparative Example 1 corresponds to an existing zinc alloy, ILZRO 14.

[0020] Cold chamber die casting was carried out using the molten metals of these zinc alloys. The casting were carried out under the following conditions: molten metal temperature: 470 to 550 °C ; mold temperature: 150 °C ; locking force: 35 tons; filling pressure: 80 kgf/cm², to thus produce each piece for creep test having an original gauge length of 50 mm and a diameter of parallel portion of 6 mm $\varnothing$.

[0021] Creep tests were carried out using these test pieces at an atmospheric temperature of 175 °C and a test load of 25 MPa, according to JIS Z 2271 to thus determine creep strains (%). The creep strains observed after 100 hours were determined. The results obtained are listed in Table 1. Moreover, the zinc alloys produced in Example 1 and Comparative Example 1 each were inspected for any change in creep strains with time. The results obtained are plotted on Fig. 1.

Table 1

	Composition (% by weight)						Creep Strain (%)
	M n	N i	C u	A l	T i	the others	
Com. Ex. 1	—	—	1.2	0.02	0.2	—	0.50
Example 1	1.0	—	—	0.02	0.2	—	0.22
Example 2	3.0	—	—	0.02	—	—	0.13
Example 3	0.5	0.5	0.5	0.02	—	—	0.17
Example 4	—	3.0	—	0.02	—	—	0.13
Example 5	1.0	1.0	—	0.02	—	—	0.09
Example 6	1.0	—	1.0	—	—	—	0.19
Example 7	—	1.0	1.0	—	—	0.2 Z r	0.16
Example 8	1.0	1.0	1.0	0.02	—	0.2 Z r	0.07
Example 9	1.5	1.5	—	—	—	0.2 C r	0.08
Example 10	1.5	—	1.5	—	—	0.2 L i	0.06
Example 11	—	1.5	1.5	—	—	0.2 B e	0.08
Example 12	—	1.5	1.5	0.02	0.2	0.2 M m	0.06
Example 13	1.5	1.0	0.5	0.02	—	0.2 Z r 0.2 L i	0.07
Example 14	1.5	1.0	0.5	0.02	—	0.2 S c	0.07
Example 15	0.5	0.5	—	0.02	—	0.05M g	0.20
Example 16	1.0	1.0	0.5	—	—	0.2 Y	0.09
Com. Ex. 2	4.0	—	—	0.02	0.2	—	Note
Com. Ex. 3	—	4.0	—	0.02	0.2	—	Note

Note: The flowability of the molten metals are low.

[0022] The data listed in Table 1 clearly indicate that the zinc alloys produced in Examples 1 to 16 according to the present invention have low creep strains as determined at a test temperature of 175°C as compared with that observed for the zinc alloy produced in Comparative Example 1, i.e., an existing zinc alloy ILZRO 14.

[0023] On the other hand, the zinc alloys of Comparative Examples 2 and 3 whose compositions are beyond the limits of the present invention have poor castability and do not form acceptable castings, since the content of nickel and manganese thereof are high and accordingly, the flowability of the molten metals thereof are low.

[0024] The data plotted on Fig. 1 also clearly indicate that the zinc alloy of Example 1 is significantly improved in the creep characteristics as determined under a test temperature of 175°C and a test load of 25 MPa as compared with those observed for the zinc alloy of Comparative Example 1.

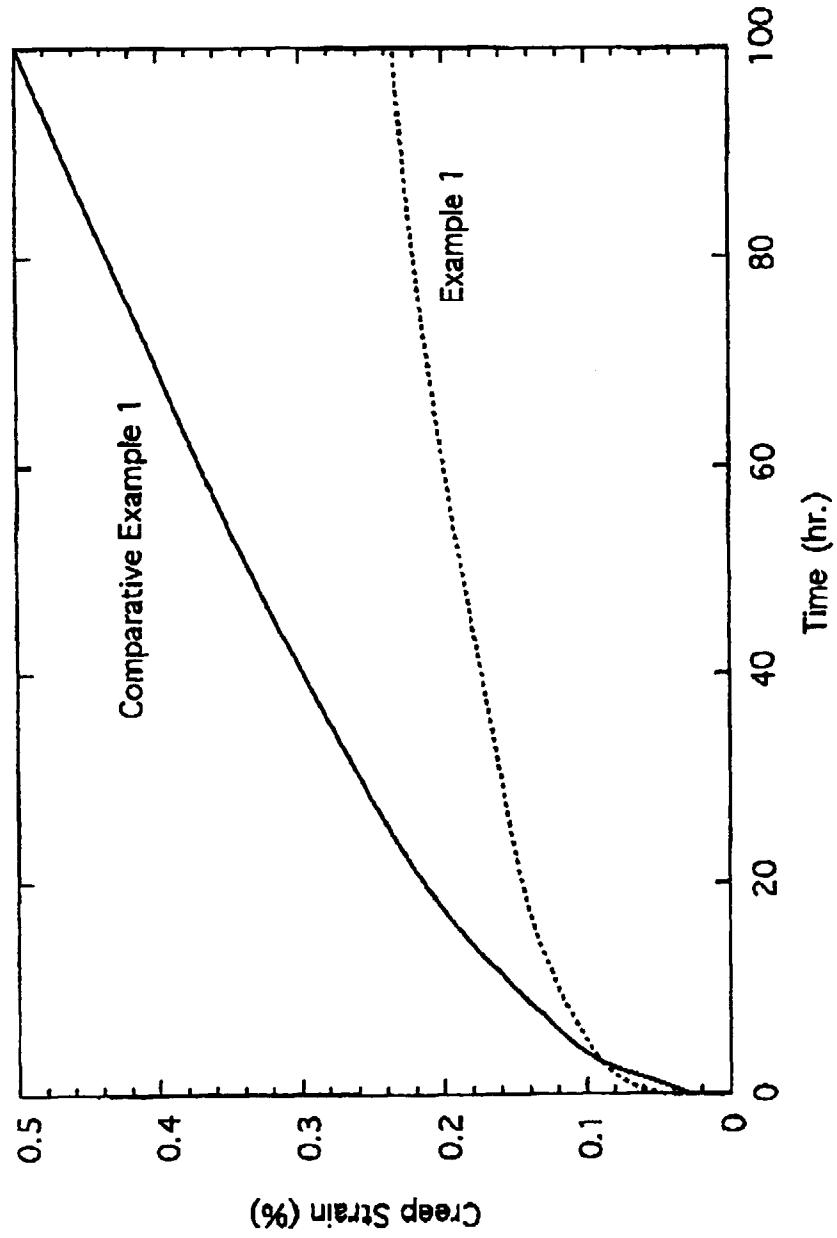
[0025] As has been explained above in detail, the heat-resistant zinc alloy of the present invention is excellent in the

creep resistance at a high temperature and thus the present invention can considerably expand the fields of application of molded articles of zinc alloys.

Claims

1. A heat-resistant zinc alloy exhibiting good creep resistance at a temperature of not less than 100 °C, comprising at least one of nickel and manganese in a total amount of not more than 3.5% by weight based on the total weight of the alloy and the balance of zinc and inevitable impurities.
2. The heat-resistant zinc alloy of claim 1 wherein it comprises at least one of nickel and manganese in a total amount ranging from 0.7 to 3% by weight based on the total weight of the alloy.
3. The heat-resistant zinc alloy of claim 1 wherein it further comprises not more than 2% by weight, based on the total weight of the alloy, of copper.
4. The heat-resistant zinc alloy of claim 1 wherein it further comprises at least one of titanium and zirconium in a total amount of not more than 2% by weight based on the total weight of the alloy.
5. The heat-resistant zinc alloy of claim 1 wherein it further comprises not more than 0.5% by weight, based on the total weight of the alloy, of aluminum.
6. The heat-resistant zinc alloy of claim 1 wherein it further comprises at least one member selected from the group consisting of chromium, scandium, beryllium, lithium, yttrium, lanthanoid and magnesium in a total amount of not more than 0.5% by weight based on the total weight of the alloy.
7. The heat-resistant zinc alloy of claim 1 wherein it further comprises at least two of the following components (a) to (d):
 - (a) not more than 2% by weight, based on the total weight of the alloy, of copper;
 - (b) at least one of titanium and zirconium in a total amount of not more than 2% by weight based on the total weight of the alloy;
 - (c) not more than 0.5% by weight, based on the total weight of the alloy, of aluminum; and
 - (d) at least one member selected from the group consisting of chromium, scandium, beryllium, lithium, yttrium, lanthanoid and magnesium in a total amount of not more than 0.5% by weight based on the total weight of the alloy.
8. A molded article comprising the heat-resistant zinc alloy as set forth in any one of claims 1 to 7.

FIG. 1





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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	FR 2 083 866 A (METALLGESELLSCHAFT AG) 17 December 1971 * page 2, line 16 - line 38; example 2 *	1-8	C22C18/00
X	GB 2 066 853 A (CENTRE RECH METALLURGIQUE) 15 July 1981 * page 1, line 9 - line 13 * * page 1, line 21 - line 29 * * page 2, line 4 - line 10; figure 1 *	1-3,5-8	
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 006, 30 June 1997 & JP 09 041057 A (MITSUI MINING & SMELTING CO LTD), 10 February 1997 * abstract *	1-8	
X	BE 775 207 A (METALLURG CT VOOR RESEARCH IND) 10 May 1972 * page 2, paragraph 1 - paragraph 3 * * page 3, paragraph 2 - paragraph 3 *	1-8	
A	FR 2 366 370 A (CENTRE RECH METALLURGIQUE) 28 April 1978 * page 2, line 14 - line 24 *	1-8	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C22C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 9 December 1998	Examiner L111mpak1s, E
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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09-12-1998

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2083866 A	17-12-1971	BE 762290 A DE 2010870 A NL 7101620 A	01-07-1971 30-09-1971 09-09-1971
GB 2066853 A	15-07-1981	BE 880406 A DE 3043488 A	01-04-1980 19-06-1981
BE 775207 A	10-05-1972	NONE	
FR 2366370 A	28-04-1978	BE 846899 A	31-01-1977

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